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T Windowless X-ray Tube Spectrometer for Light Element Analysis*

[Ralph W. G. Wyckoff and Franklin D. Davidson] [1963] 13 p refs

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A windowless tube spectrometer is described for the x-ray "fluorescent" analysis of the light elements down through fluorine. The high efficiency of x-ray excitation makes possible the analysis of elements as light as sodium when present in less than 1 % and of fluorine in larger amounts.

AUTHOR

It has earlier been shown¹ that for the lighter chemical elements the yield of "fluorescent" x-rays is greatly increased by

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eliminating a window between the primary x ray target and the sample. Since weakness of the fluorescent excitation of silicon and aluminum, and still more so of magnesium and sodium has set severe limits to the x-ray spectroscopic analysis of these elements, such an increase in the efficiency with which their characteristic radiations can be excited permits a significant extension of practical spectroscopy. The previous observations were not made with an apparatus intended as a fluorescent spectrometer. A simple instrument has since been developed and is being routinely used for the study of the light elements in rocks and in a variety of materials of biological origin. It is described below and measurements given to indicate the range of its usefulness.

METHODS

The apparatus consists of a demountable x-ray tube and an attached sample chamber and spectrometer (Fig. 1). The tube is a modification of a gas tube described² a generation ago; the spectrometer is a standard Philips diffractometer altered for helium-path operation.

The x-ray tube is one that can be used for either gas or hot-filament operation by merely exchanging the cathode. As a gas tube it is employed in much of the soft x-ray work being carried out in this laboratory. With its inexpensive pumping system it provides an x-ray source constant enough for quantitative x ray spectroscopy;

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and its target, unlike that of a demountable hot-filament tube, does not rapidly contaminate. Such spectral purity is unnecessary for fluorescent excitation, however, and both types of cathode have proved satisfactory and given substantially the same "fluorescent" yields in the present apparatus. It is pointless to put more than 200 W through the tube; this simplifies its construction and permits the use of a relatively cheap power supply (F of Fig. 1). The grounded anode (t) and tube block (G) should be water-cooled but either cathode (C) is sufficiently cooled by blowing air against an attached set of copper fins. When a hot filament is used a Coolidge transformer must, of course, be added to heat it. High voltage insulation is obtained by supporting the cathodes on lengths of pyrex drainage tubing. The x ray protection this fails to supply is given by surrounding it with a double leucite cylinder filled with BaSO_4 (B). Measurements reported earlier have shown that with windowless operation the "fluorescent" output depends very little on the anode of the tube. In the present experiments this anode was of gold.

The sample chamber (H) is a separate unit attached to the tube block through an O-ring seal. The sample is held in a removable coned fitting (s) which, like the chamber, requires no cooling. The sample is 2 1/2 in. distant from the primary target and has an unobstructed "view" of it through a 1/2 in. hole in the tube block. For most of our work the sample is a compressed 1 in. pellet. When a pure powder does not cohere under pressure, 10 % boric acid or graphite has been added as binder. Such admixture does not interfere with the analysis of even as light an element as sodium. In windowless operation the tube must be opened to the air for change of sample; the five minutes required for this could be reduced by

redesign of the pumping system.

Spectrometers for the wave length region considered here have had either a vacuum or a helium (or hydrogen) path. This instrument is of the latter type. The window to separate the vacuum of the sample chamber from the helium path of the spectrometer, of 0.15 mil Mylar, is placed on the crystal side of the entrance Soller slit (a). This positioning is essential; so thin a window mounted on the sample side of the slit is quickly destroyed even if coated with a conducting aluminum layer. To minimize x ray absorption the counter window must be the thinnest that will serve as an effective barrier between the gas of the counter and the helium of the spectrometer. Since with a helium path there is no pressure differential, a collodion or formvar film of the sort used as substrate in electron microscopy is satisfactory. It is mounted as the front window of a proportional counter filled with P-10 gas (E). The chamber (D) has a removable leucite fact to permit easy exchange of crystals. Potassium acid phthalate is the best available reflector for the elements considered here, and there is complete spectral separation except that its long spacing ($2d = 26.8 \text{ \AA.}$) causes a slight overlap between aluminum and silicon. For most accurate results with these two elements and for shorter x rays, mica or gypsum is preferable. A stacked monomolecular film "grating" can be used for magnesium and longer wave lengths. For this radiation a "grating" consisting of 150 layers of barium stearate ($2d = \text{ca } 100 \text{ \AA.}$) reflects with one third the efficiency of potassium acid phthalate.

This spectrometer is now being used for elements down through fluorine. Two factors which together set the limit of sensitivity for the analysis of a particular element are (1) the intensity of the spectral peak and (2) its peak-to-background ratio. In what follows, intensities are generally expressed as efficiencies of excitation, i.e. counts per second per watt (c/s/w), and unless especially noted, the peak-to-background ratios (p/b) are the crude counts not improved by a pulse height suppression of background. The efficiencies, of course, depend on many variables such as applied voltage, perfection of alignment and crystal analyzer; those given are typical of the performance of this instrument when used routinely. Similarly no absolute significance attaches to the stated values of p/b; they depend on the same factors that influence efficiency and above all on the composition of the sample.

As expected, the efficiencies measured with this spectrometer are much higher than with the preliminary equipment. Thus, with 100 W input at 20kv, pure aluminum gives a K- α peak reading of 15,300 c/s. This efficiency of 153 c/s/w is to be compared with the 3.4 c/s/w measured with the early apparatus and the ca 0.1 c/s/w measured (with an EDDT crystal) in a commercial Philips vacuum spectrometer. Such a 1500 times improvement over the commercial equipment is exceeded for magnesium and sodium; for pure magnesium the c/s/w in the present spectrometer is 90. For both metals the p/b ratio exceeds 100. A corresponding efficiency for pure sodium has not been measured but it can be estimated as ca 21 c/s/w by extrapolating the straight line calibration (Fig. 2) made by diluting

Na_2CO_3 with silica. Evidently such high yields of characteristic radiation offer new possibilities for the analysis of these light elements.

To evaluate them a series of standardizations were made using samples containing diminishing amounts of aluminum, magnesium and sodium, the diluent being silica. Three of these curves are collected in Fig. 3. They illustrate the fact that with a tube input not exceeding 200 W the counts obtained are adequate for measuring fractions of a percent even of sodium in silicious materials.

Simple calibration curves such as these give an approximate knowledge of the composition of rock though, of course, much better standards and a detailed matrix correction would be required for results of the highest attainable accuracy. As an example of the data supplied by this instrument, measurements are given on a triassic diabase (Bureau of Standards radioactive sample No. 4984). Its approximate content of the metallic elements in question (and not of their oxides) is Si: 21.9 %, Al: 7.5 %, Mg: 3.5 % and Na: 1.5 %. The counts from a sample consisting of 90 % diabase, 10 % boric acid were Si: 6,575 c/s, Al: 2,000 c/s, Mg: 400 c/s and Na: 85 c/s, the tube being operated at 200 W. This diabase contains amounts of iron and calcium sufficient to produce a definite matrix effect; nevertheless, a direct reading from the charts of Figure 3 leads to the composition Si: 24.0 %, Al: 6.0 %, Mg: 1.6 % and Na: 1.8 %. Results of similar accuracy are being obtained from the many rocks being analyzed.

The p/b ratio necessarily becomes poorer the less there is of an element in a sample and the lower the atomic number. For pure Na_2CO_3 p/b = 15. As an example of the effect of pulse height discrimination in this part of the spectrum a silica-based sample containing 1.0 % Na gave a peak with p/b = 1.5; with pulse height discrimination this ratio had improved to 3.5 with few sodium counts lost.

The Mylar window is the most absorbing element in the x-ray path of this spectrometer and it, rather than the crystal, sets the long wave length limit to its use. The high counts with sodium have made it seem worthwhile to see if fluorine, which has never been detected with any of the commercial x-ray spectrometers, could be analyzed. The peak recorded at 200 W from a sample of lithium fluoride using a potassium acid phthalate crystal is shown in Fig. 4; with pulse height this background is reduced from ca 45 c/s to only ca 3 c/s. Measurements on standards containing decreasing amounts of fluorine indicate that ca 5 % fluorine is the minimum which can be analyzed with this spectrometer.

DISCUSSION

The very high yields of characteristic x rays obtained through windowless operation are largely due to sample bombardment by electrons scattered by the anode. This naturally raised the question of whether or not still better results would be achieved by recourse to the more efficient direct excitation to be expected when the sample is the target of the x ray tube. This was routinely done in

the early days of qualitative x ray spectroscopy. Large nonconducting samples as anodes, however, result in a tube operation too irregular for convenient quantitative analysis and if they are of the lighter elements the contamination that rapidly builds up on them steadily diminishes the x ray output. Such difficulties are avoided through the mixed fluorescent excitation used here. Charging up of the sample or its contamination has never been observed even after prolonged irradiation. Windowless operation has the further advantage of assuring the uniform sample irradiation without observable decomposition which is essential in dealing with samples like rocks that vary in composition from point to point.

Footnotes

1. R. W. G. Wyckoff and F. D. Davidson, Rev. Sci. Instr. 34, 572 (1963).
2. R. W. G. Wyckoff and J. B. Lagsdin, Rev. Sci. Instr. 7, 35 (1936).

Figures

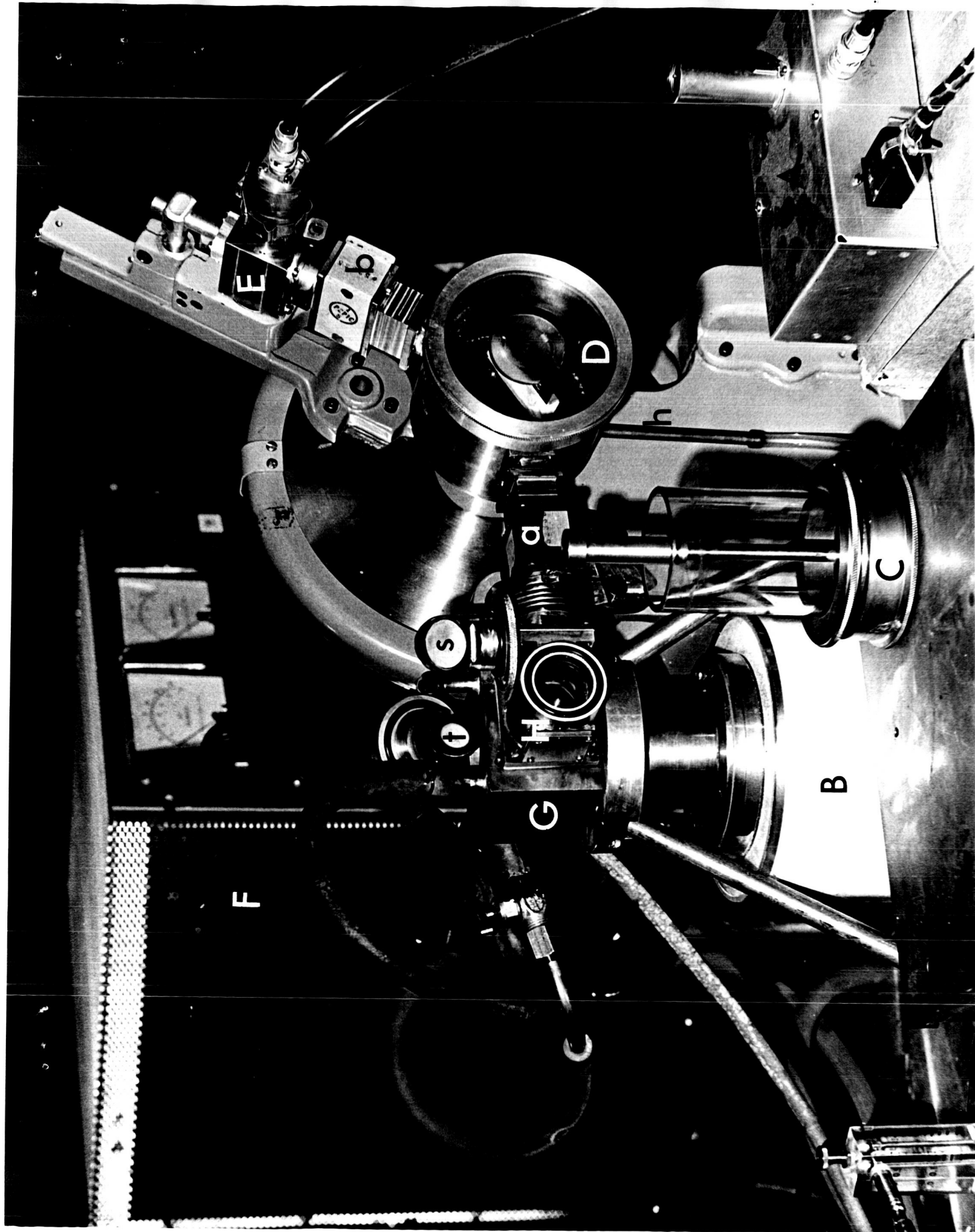
Figure 1. A photograph of the windowless x-ray spectrometer.

Most letters are referred to in the text but in addition (h) is the helium inlet and (A) the preamplifier for the counter.

Figure 2. A calibration curve prepared from silicious mixtures containing up to 20 % sodium with 200 W (20kv) across the tube.

Figure 3. Calibration curves from silicious mixtures containing up to 20 % aluminum, magnesium and sodium with 200 W (20kv) across the tube. The corresponding curve for silicon is not shown but a 20 % silicon sample will, under these conditions, give ca 7000 c/s and a 40 % sample ca 14,000 c/s.

Figure 4. The fluorine peak obtained from LiF with 200 W (20kv) across the tube.



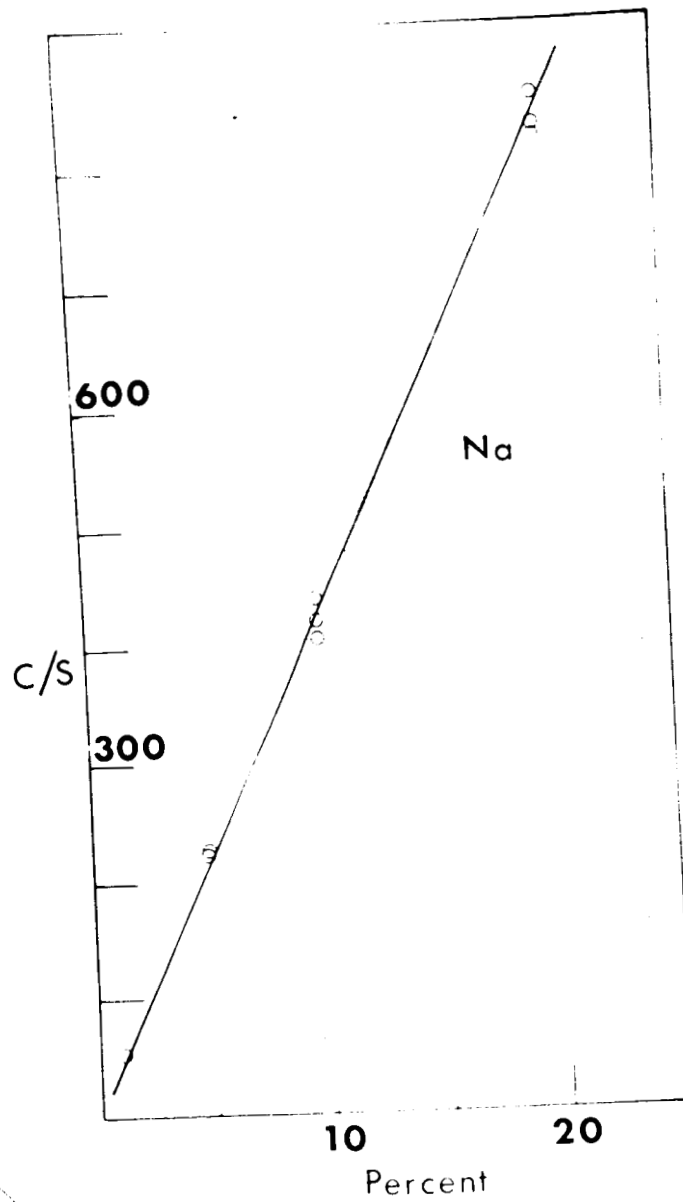


Figure 2

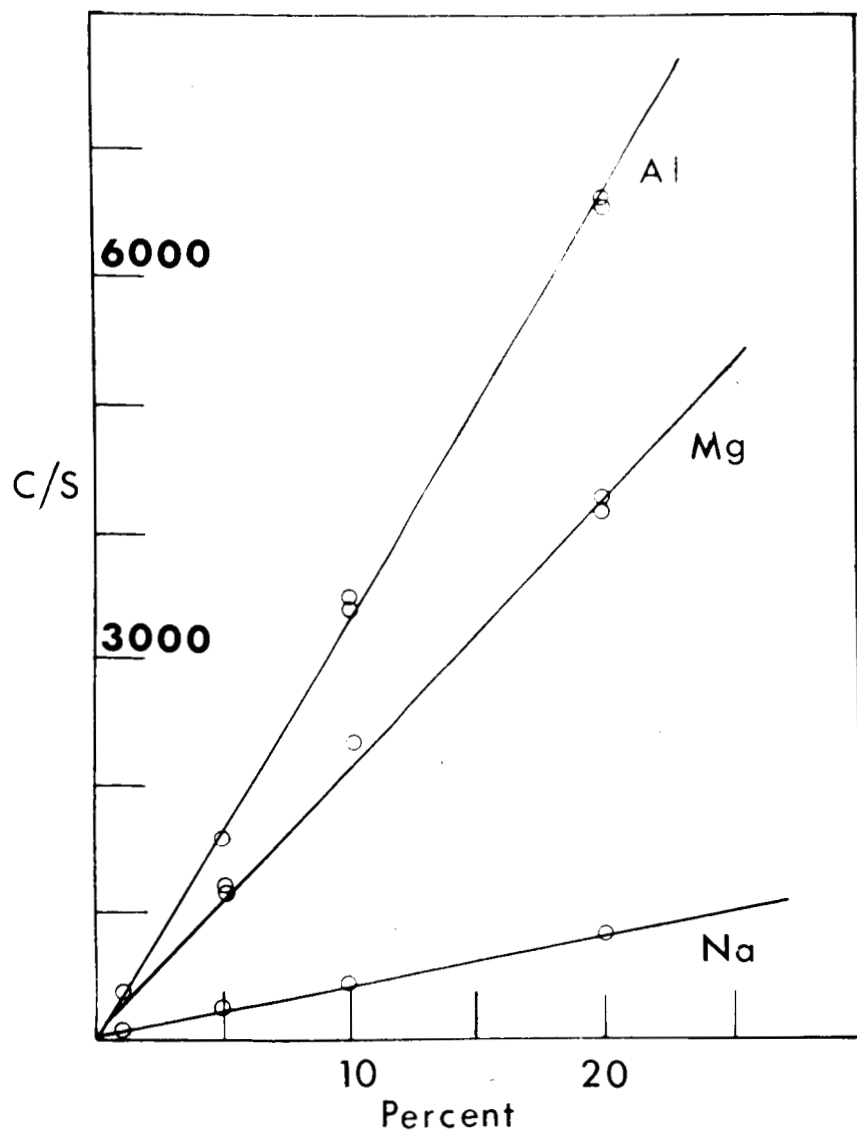


Figure 3

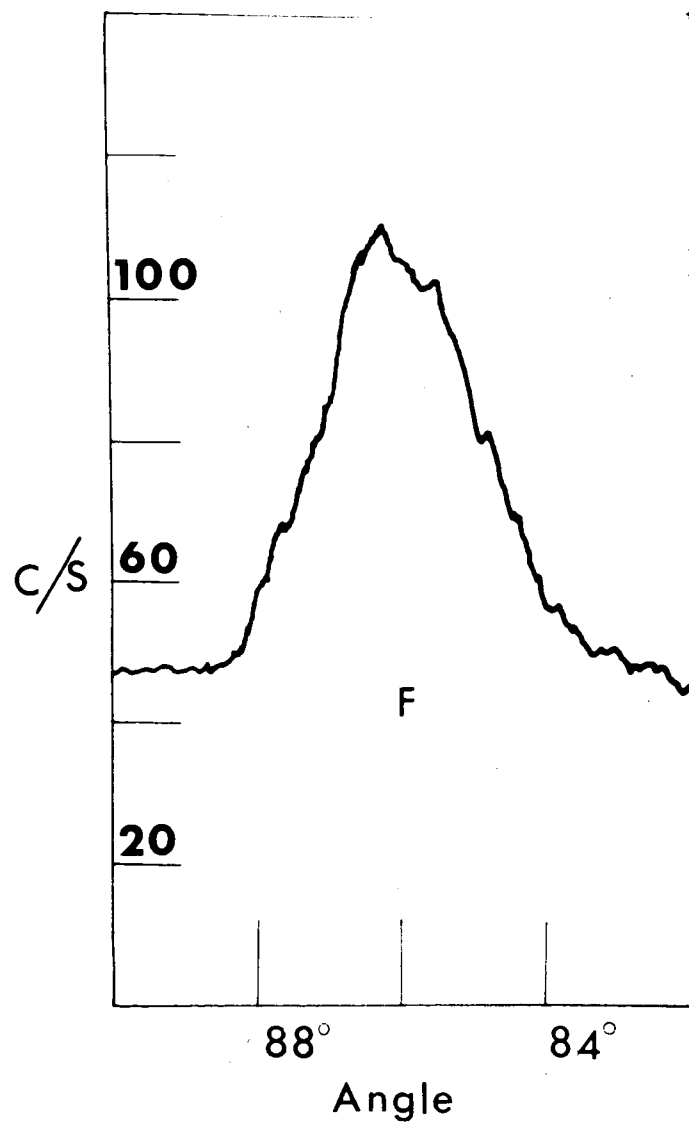


Figure 4